

The Attainable Superheat: from Simple to Polymeric Liquids ¹

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ABSTRACT

The phenomenon of the attainable superheat of a substance and the kinetics of nucleation of a vapor phase have been studied experimentally for liquids with molecular weight from 10^2 to 10^4 . The values of the temperature of spontaneous boiling-up T^* have been measured in a wide range of parameters (pressure, heating rate, CO_2 content, molecular chain length and thermal stability of a substance) by the method of controlled pulse heating of a thin wire probe using pulse lengths from 0.01 to 1 ms. The investigation is based on a gradual increase of the molecular weight of a sample. The peculiarities of spontaneous nucleation in polymeric liquids that do not boil without decomposition are discussed. It is shown that this phenomenon is a reproducible relaxation process in a polymeric system, which accompanies the initial stage of its thermal decomposition.

KEYWORDS: controlled pulse heating; mean lifetime; polymeric liquids and oils; spontaneous boiling-up; thermal decomposition.

1. INTRODUCTION

In ordinary practice we observe boiling-up on artificial (heterogeneous) vapor formation centers. As the rate of crossing the line of liquid-vapor equilibrium $T_s(p)$ increases, a higher supersaturation of liquid $T - T_s$ is achieved, and the contribution of the bubbles of spontaneous origin to the vapor generation increases. We shall consider the phenomenon of spontaneous boiling-up of highly superheated liquids that occurs at sufficiently rapid heating. In this case one can break through the background of heterogeneous nucleation and achieve the limiting values of superheat predicted by the homogeneous nucleation theory [1, 2]. It is significant that the process of spontaneous boiling-up is characterized by the reproducibility and by the high slope of the $J(T)$ dependence, where J is the nucleation rate of viable bubbles. This provides a basis for unambiguous detection of the spontaneous boiling-up moment by a certain experimental feature.

The spontaneous boiling-up kinetics and the related phenomenon of attainable superheat of a substance with respect to the liquid-vapor equilibrium temperature have been studied in detail for simple liquids and their solutions [3, 4]. For them the reliable methods of observation of the initial stage of boiling-up have been developed. The results of the experiments agree with the calculation of $J = J(T, p)$ based on the homogeneous nucleation theory with the work of the critical bubble formation written in the thermodynamic approximation. The description of this phase transition becomes less evident as a molecular-chain length increases up to several tens (and hundreds) of links. The complication does not originate solely from the difference in the properties of high-molecular-weight liquids and their low-molecular-weight analogs. It is clear that at a certain step of the chain length increment the boiling-up temperature of a substance will exceed the onset temperature of the thermal decomposition of macromolecules.

The difficulty of the very formulation of the problem is that a rapid heating of a polymeric liquid transforms it into a multicomponent system with the time-dependent composition and the time-dependent value of the work of the critical bubble formation $W_* = W_*(T, p, t)$. This circumstance complicates a direct application of the homogeneous nucleation theory and the equations of state to the description of this phase transition. In such

conditions a systematic experimental investigation of the phenomenon of spontaneous bubble nucleation in a wide range of molecular weight of the samples appears to be timely. The emphasis is made on the elucidation of the peculiarities of this process for polymeric liquids. The specific feature of the object originates from the fact that macromolecules cannot form the vapor phase without their decomposition.

An appropriate choice of the method is crucial for solving the problem. Our experience suggests that a distinct signal of vaporization in polymeric liquids may be resolved only in the regime of sufficiently rapid heating [5]. Moreover, an investigation of the phase transition in a polymer retaining the substance individuality makes sense only at small degrees of decomposition, which is equivalent to short heating times.

2. EXPERIMENTAL

We used the method of pulse Joule heating of a thin wire probe in a substance [1, 3]. The method allows to achieve a controlled superheat of the probed layer of liquid, to detect the characteristic boiling-up signal on the heating curve and to determine the substance temperature (by the probe resistance) at any moments we are interested in. In our experiments the average heating rate was from 10^5 to 10^7 K/s, which corresponded to the duration of heating of a substance before its boiling-up t^* from 10^3 to 10^1 μ s.

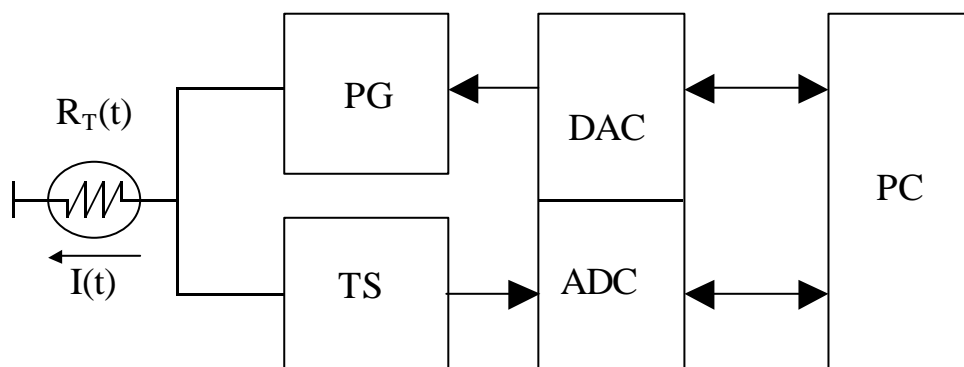


Fig. 1. Block diagram of the apparatus: DAC, digital-to-analog converter; PG, pulse generator; R_T , probe; TS, tracking system; ADC, analog-to-digital converter.

The method is illustrated by the schematic block diagram of the apparatus presented in Fig.1. Its main element is a platinum wire probe with diameter of 10 μ m. This probe combines a heater and a resistance thermometer. The whole process of variation of the probe

temperature in a continuous liquid and then in a boiling layer is recorded. The characteristic break on the time dependence of the probe temperature $T(t)$, see Fig. 2, corresponds to the moment of formation of vapor bubbles at its surface. The heat flux into the liquid, the moment and the temperature of boiling-up, and the probe temperature perturbation caused by boiling-up are determined experimentally. These parameters are important for establishing the peculiarities of heat transfer in the pulse-heated liquid before and after its boiling-up. However, this is the subject of a separate discussion. Here we shall concentrate on the temperature and time conditions of the spontaneous boiling-up phenomenon.

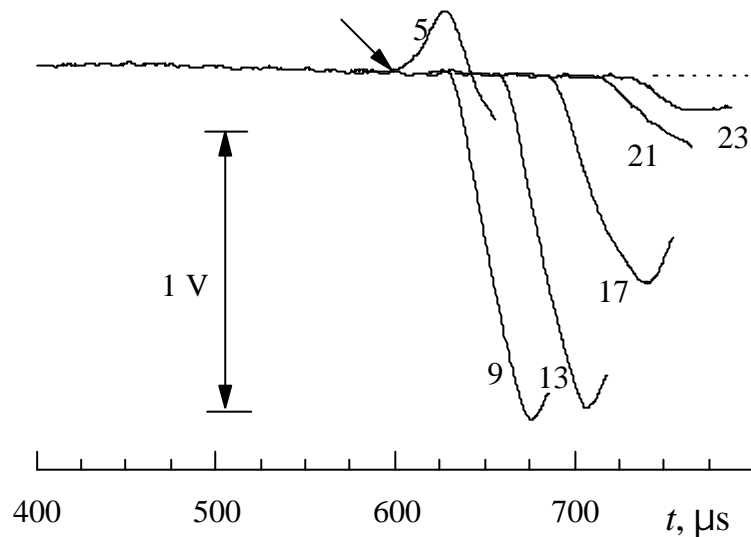


Fig. 2. The boiling-up signals separated from the background of smooth heating for CO_2 solution in the oil "Mobil SAE 5W-50" at different pressures and heating rate $\dot{T} \approx 0.7 \text{ K}/\mu\text{s}$. The indicated numbers are the pressure values in bars. The arrow shows the point of boiling-up for $p = 5 \text{ bar}$.

By the temperature perturbation $Q(t - t^*)$, see Fig. 3, we mean the difference between the actual probe temperature and its extrapolated value into the region $t > t^*$ assuming that there is no boiling-up. In order to get the necessary resolution of the initial stage of the process, the useful temperature perturbation signal was separated from the background of large average values of electrical quantities tracked in experiment, and this signal was amplified. The details regarding the construction and operation of the measurement system are given elsewhere [6].

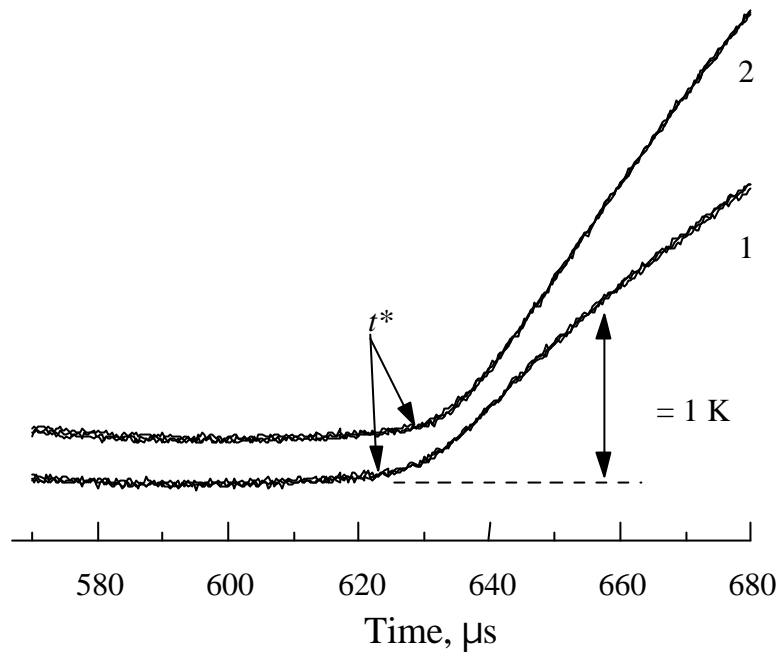


Fig. 3. The probe temperature perturbation $Q(t - t^*)$ caused by boiling-up of poly(dimethylsiloxane) PDMS-10000 at pressures 0.03 MPa (curves 1) and 0.01 MPa (curves 2). Superposition of 3 sequential pulses is shown for the both cases.

In order to improve the reliability of our conclusions concerning the kinetics of spontaneous nucleation in a polymeric liquid and the contribution of the process of thermal decomposition to its onset, we have developed a procedure for setting the required (in the general case, arbitrary) regime of heating. This procedure allows to choose and finely control the probe heating profile $T(t)$ in a series of measurements taking into account a number of the thermal properties of the sample.

The objects of our studies were the following substances: homological series of polystyrene, poly(ethylene oxide), and polydimethylsiloxane with a chain length from one to several hundreds of links; polymer melts of different structure; polymer solutions in standard solvents. The solutions of carbon dioxide in solvents and polymers were chosen as model systems. Measurements have been made in a wide range of variables: the concentration c , the pressure p and the sample heating profile. Investigation has been carried out in order of increasing object complexity - from a simple liquid to a polymer melt.

3. RESULTS AND DISCUSSION

In experiments on polymer-solvent systems the aim was to elucidate the peculiarities of boiling-up of such systems in the full range of compositions. By solving this problem, one can make a smooth transition to measurements on pure polymers. The results of the experiments are summarized in Fig. 4. Let us emphasize the essential result providing a foundation for the development of this investigation. We have revealed that for changes of the solution composition from a pure solvent to a polymer melt the characteristic signal of boiling-up retains the confinement in time and the reproducibility with respect to temperature, as typical of the spontaneous mechanism, see Fig. 3. The differences manifest themselves only in quantitative characteristics of this signal, $Q(p, t - t^*)$. This indicates that at the heating rates $\dot{T} \sim (10^5 - 10^7)$ K/s the degree of superheat of both low-molecular-weight and high-molecular-weight systems is close to its limiting value, which corresponds to a high nucleation rate.

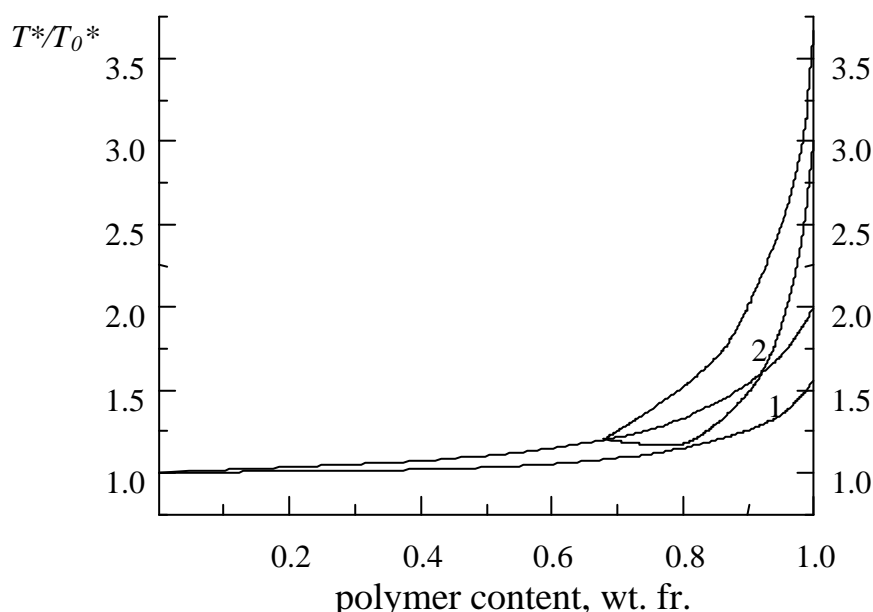
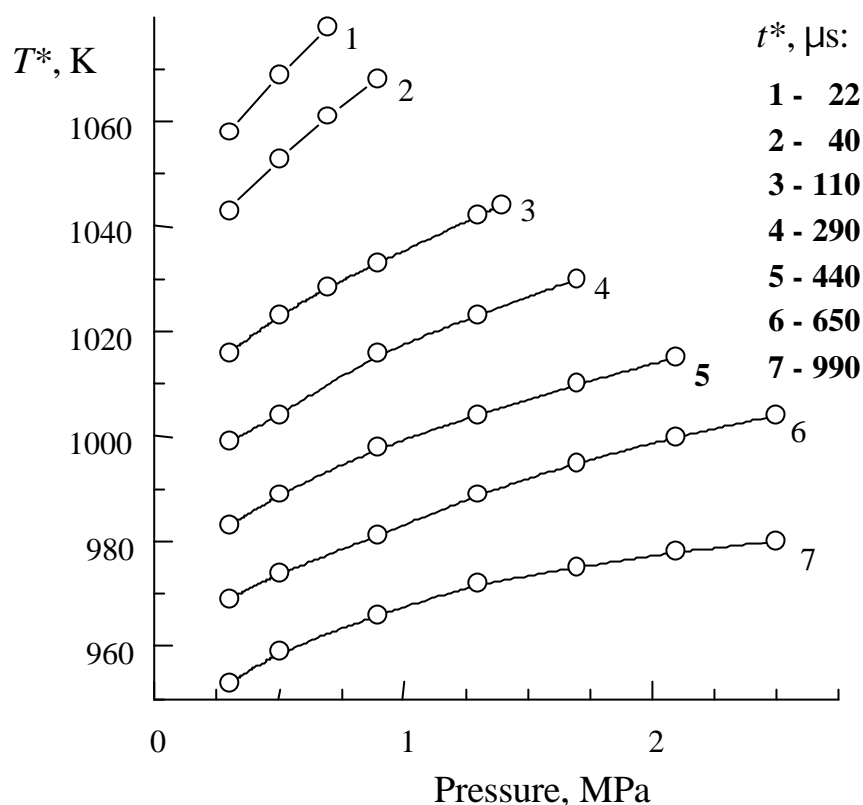


Fig. 4. Generalization of the results on spontaneous boiling-up temperature for polymer-solvent systems reduced to that of the solvent vs. polymer weight fraction. The regions characteristic for standard solvents (1) and for carbon dioxide (2) are shown. The values of T_0^* vary from 277 K ($p = 1$ MPa) for carbon dioxide to 685 K ($p = 0.5$ MPa) for diethylene glycol.



For low solvent contents ($1 - c \rightarrow 0$) the values of the temperature of spontaneous boiling-up T^* increase sharply going deeper into the region of thermal instability of the components. This is accompanied by enhancement of the $T^*(\dot{T})$ dependence, see Fig. 5 for oligodivinyliisoprene ($M_n = 4.5 \cdot 10^3$), as typical of thermally unstable compounds. The slope of this dependence is determined by the kinetics of the thermodecomposition reaction, the composition of volatile products and the degree of their compatibility. Measurements on model systems (hexadecane + CO_2 , tetraethylene glycol + CO_2) with systematic variations of the thermodynamic stability of the solution have shown that a decrease in the stability is equivalent to an increase in the solvent content in the initial system.

In experiments on polymer homologs with narrow molecular weight distributions $M_w/M_n \sim (1.01 - 1.19)$, the aim was to elucidate the peculiarities of vapor nucleation with increasing chain length from several links to several hundreds of links. The temperature T^* and the temperature perturbation $Q(t - t^*)$ have been measured as functions of the pressure at different heating rates. The pressure increased up to the effective critical pressure, at which the response signal was no longer resolved, i.e. $Q(p \rightarrow p_c^*) \rightarrow 0$, where $p_c^* = p_c(t^*)$.

It has been found that the temperature T^* for the low-molecular-weight homologs increases rapidly with increasing chain length. The main increase in T^* is observed in the region $M_n < 1 \cdot 10^3$ or $n < 10$ links and 20 links, respectively, for polystyrene and poly(ethylene oxide). As the chain length increases further, the dependence of $T^*(M_n)$ tends to level off [7]. The limiting value of $T^*(M_n)$ increases with increasing pressure, see Fig 6, and with increasing heating rate. We connect the plateau in the $T^*(M_n)$ dependence with the onset of the decomposition of macromolecules before their transition into the vapor phase. The increase of the effective critical pressure along the $T^*(M_n)$ plateau, see Fig. 6, supports this hypothesis. According to the investigation made on model systems ($C_nH_{2n+2} + CO_2$ with different CO_2 content, $n \sim 5-16$), this increase is caused by the formation of a low-molecular-weight component in the course of heating.

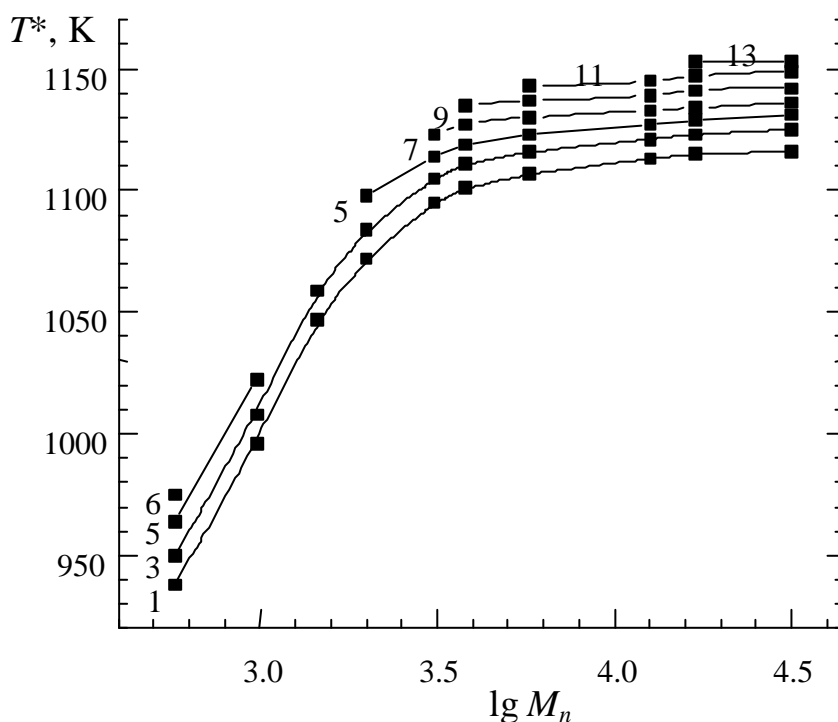


Fig. 6. Temperature of spontaneous boiling-up of poly(ethylene oxide) vs. number-average molecular weight at different pressures. The indicated numbers are p values in bars. $t^* = 22 \mu s$.

It is important to complement the results obtained for these series and solutions of polymers with the data for polymeric samples of different nature. For this purpose the

dependence of $T^*(p, \dot{T})$ was measured for several commercial grade polymers. The experiments have shown that the dependences of $T^*(p)$ at a given heating rate are grouped in a relatively narrow temperature range, see Fig. 7. For comparison, the corresponding values for low-molecular-weight analogs are scattered over several hundreds of degrees.

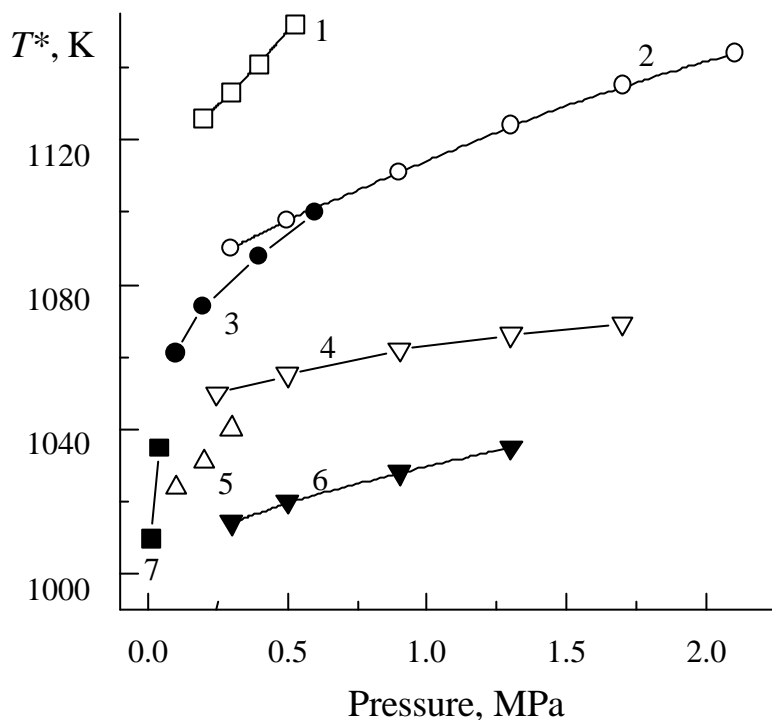


Fig. 7. Temperature of spontaneous boiling-up of polymer melts vs. pressure for heating time $t^* = 110 \mu\text{s}$. 1 - polyethylene, 2 - polyurethane, 3 - polypropylene, 4 - polystyrene PS-35000, 5 - polypropylene oxide ($M_n = 5 \cdot 10^3$), 6 - oligobutadiennitril (OBD-resin, $M_n = 3.5 \cdot 10^3$), 7 - poly (dimethylsiloxane) PDMS-10000.

In spite of the known differences in quantitative characteristics of the thermal decomposition of polymers and in the T^* values of their low-molecular-weight analogs, the differences in the values of $T^*(\dot{T} = \text{const})$ for the studied polymers appear to be small. The temperature T^* of a polymeric liquid is determined mainly by the slope of the temperature dependence of the thermodecomposition process at the temperature and time conditions characteristic of our experiments; the dependence of T^* on the thermodynamical properties of a monomeric link is weak. Evidently, a considerable decrease in the characteristic time of the

thermal decomposition with increasing temperature sets a practical limit on the upper value of $T^*(p, M_n)$ for a polymer that can be reached in experiment.

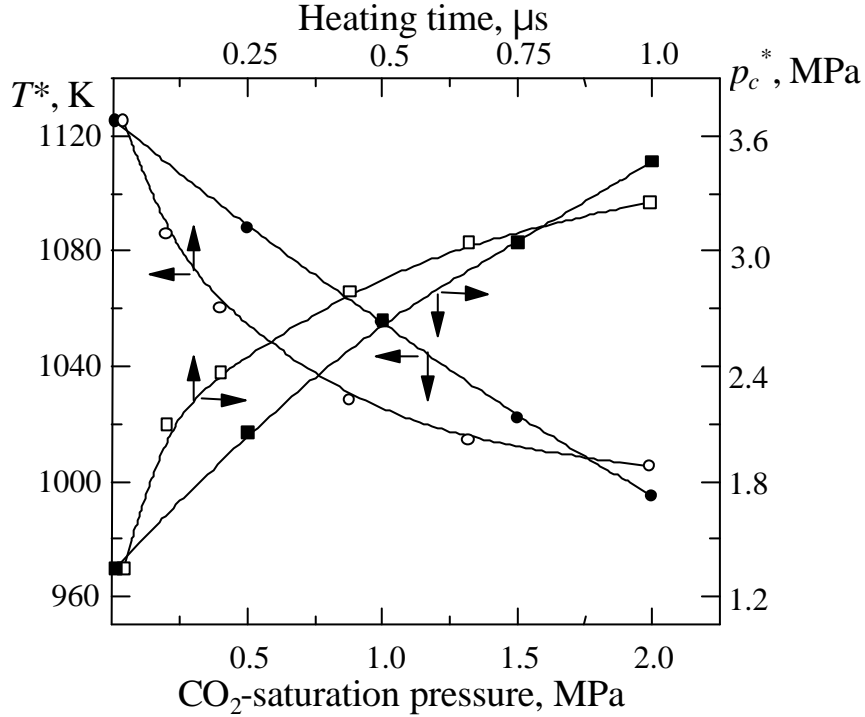


Fig. 8. Temperature of spontaneous boiling-up and effective critical pressure of poly(ethylene oxide) PEO-35000 vs. CO₂-saturation pressure (filled circles) and heating time (open circles).

The decrease in the heating rate of a polymer has proved to lead to similar effects on the characteristics of boiling-up, as the addition of a low-molecular-weight component to the system. The qualitative similarity of the dependences $T^*(p, \dot{T})$ for a polymer and $T^*(p, c)$ for a solution, see Fig. 8, suggests to use the results obtained for boiling-up of ordinary solutions for a description of the nucleation of vapor phase in polymeric liquids. Taking into account the difficulties of a quantitative description of the decomposition process at the temperature and time conditions of our experiments, it has proved possible, in the first approximation, to model the boiling-up characteristics $T^*(\dot{T})$ of a polymer by introducing a certain quantity of a low-molecular-weight additive into the melt. The use of carbon dioxide vapor for this purpose appears to be convenient, since the CO₂ content can be controlled precisely in the course of experiment by changing the vapor pressure or the solution temperature. We have revealed that quite small CO₂ content may lead to the same reduction of the T^* value as that caused by an

order of magnitude decrease in \dot{T} . For instance, for poly(ethylene oxides) this content was approximately equal to 0.01 weight fraction. The small value of this content allows to assume that a polymer mainly retains its structure at the moment of spontaneous boiling-up of dispersed thermodecomposition products. Therefore, the temperature T^* for a polymeric liquid may be indeed regarded as its individual characteristic.

In order to clarify the relation between the phenomenon of spontaneous boiling-up of a polymeric liquid and the process of its thermal decomposition, we have performed the experiments employing systematic changes of the heating profile in the region of thermal instability of a substance. As in the case of the linear heating, the value of T^* has proved to be sensitive to the change of the heating function form (function of the current through the probe $I(t)$), where $T^* = T^*[P(t)]$, $P = \dot{I}^2 \cdot R_T$, $R_T = R(T)$.

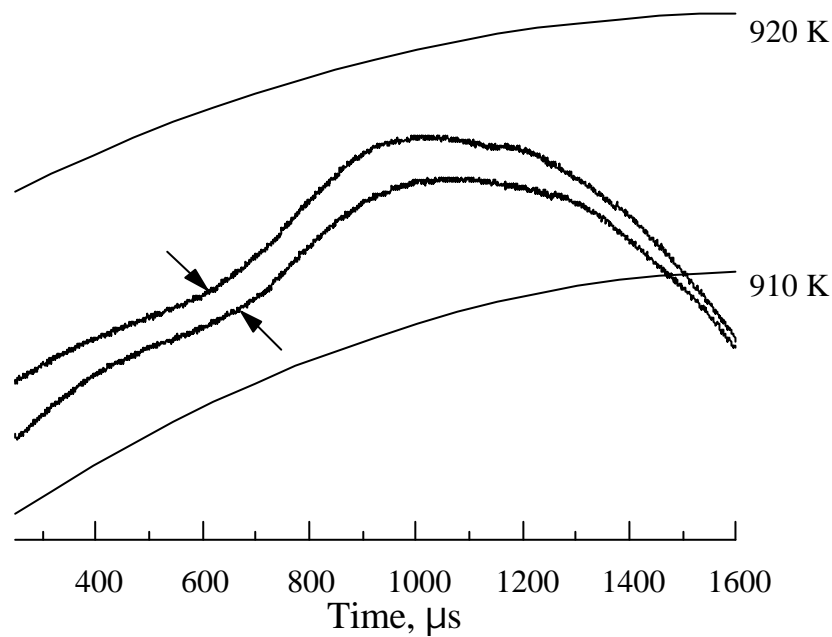


Fig. 9. Characteristic heating curves $T(t)$ in the plateau regime. The arrows show the point of oligomer boiling-up. Two isotherms show the temperature scale.

Let us consider, in particular, the regime corresponding to the heating profile that consists of linear pieces. It provides a possibility of rapid penetration into the region of thermal instability of a substance and the detailed analysis of the behavior of the system in this region. The limiting cases are the regimes of the linear heating and the temperature

plateau [6, 8]. The latter regime is of interest, since it allows to create nearly isothermal conditions $T(t > t_{pl}) \approx T_{pl}$ and to determine the mean life time of a substance $\bar{t} = \bar{t}(T_{pl})$ before its decomposition (boiling-up) at a given probe temperature T_{pl} , see Fig. 9. An increase in the slope of the dependence $\bar{t}(T_{pl})$ with increasing thermal stability of a sample has been revealed.

Characteristic results of the T^* measurements values for a polymer corresponding to different heating profiles are given in Fig. 10. The changes of the probe temperature in the time interval preceding the boiling-up are shown by the dashed lines. The points for heating profiles of the same type are connected by the solid lines.

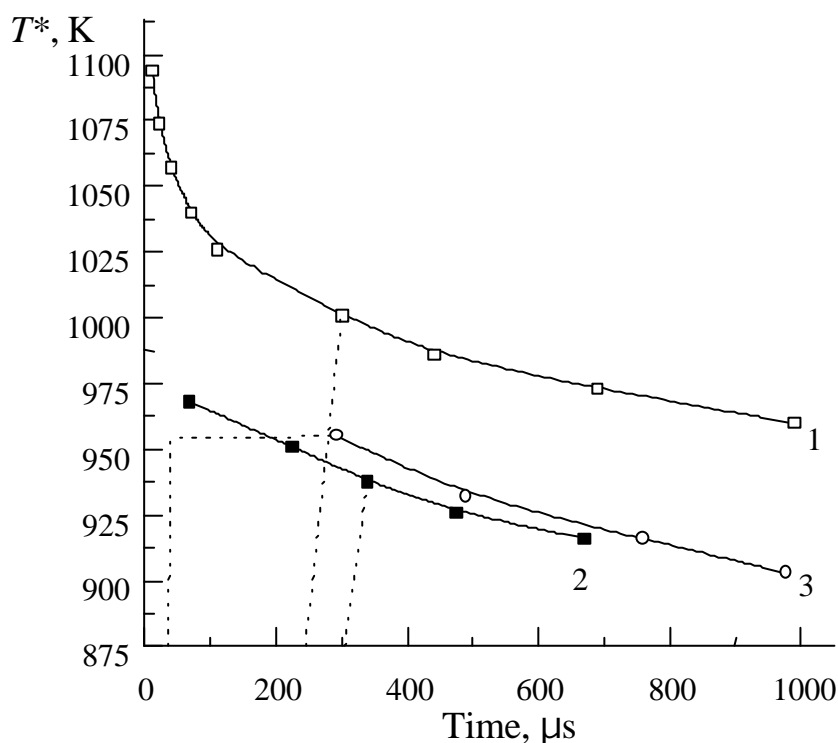


Fig. 10. Temperature of spontaneous boiling-up of OBD-resin (points 1 and 3) and CO_2 solution (0.01 wt. fr.) in this resin (points 2) vs. heating time for two heating regimes: the linear regime (1, 2) and the plateau one (3). Dotted lines show heating profiles.

The increase of the spontaneous boiling-up temperature with increasing heating rate in the region $T > T_d$, where T_d is the effective thermal decomposition temperature, has been revealed. Further studies are required, in order to determine the quantitative parameters of this relation.

The set of experimental results obtained in our experiments on systems of different nature gives the basis for the following conclusions. The spontaneous nucleation of vapor phase in polymeric liquids at the rapid heating is a reproducible process which accompanies the initial stage of the thermal decomposition of a system. Its characteristic time is much shorter than that of chemical reactions proceeding in these conditions. The reproducibility of T^* values at the given values of p , \dot{T} implies the reproducibility of relaxation processes preceding a macroscopic phase transition as well as the steepness of their temperature dependence.

4. CONCLUSIONS

The high-temperature part of the liquid–vapor phase diagram of substances with different molecular chain length has been investigated experimentally. A phenomenon of the spontaneous boiling–up of a polymeric liquid marked by a characteristic perturbation of the time dependence of the heat flux has been revealed. It is shown that this phenomenon is a reproducible relaxation process in a high molecular weight system, which accompanies the initial stage of its thermal decomposition.

The set of the experimental data agrees with the prediction of the model of rapid phase transition in pulse–heated polymers [9]. The model allows for the process of thermal decomposition, which is responsible for the very possibility of the polymer boiling–up. It describes the tendencies in the changes of the spinodal temperature (taken as an approximation for the polymer boiling–up temperature) and of the critical point coordinates caused by changes in the process conditions, the chain length of a polymer and its thermal stability.

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